Weak Magnetic Order in the Bilayered-hydrate $Na_xCoO_2 \cdot yH_2O$ Structure Probed by Co Nuclear Quadrupole Resonance — Proposed Phase Diagram in Superconducting $Na_xCoO_2 \cdot yH_2O$ —

Y. IHARA,[1*] K. ISHIDA,[1†] C. MICHIOKA,[2] M. KATO,[2] K. YOSHIMURA,[2] K. TAKADA,[3] T. SASAKI,[3] H. SAKURAI,[4] and E. TAKAYAMA-MUROMACHI[4]

[1] *Department of Physics, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan.*
[2] *Department of Chemistry, Graduate School of Science, Kyoto University, Kyoto 606-8502, Japan.*
[3] *Advanced Materials Laboratory, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan.*
[4] *Superconducting Materials Center, National Institute for Materials Science, 1-1 Namiki, Tsukuba, Ibaraki 305-0044, Japan.*

A weak magnetic order was found in a non-superconducting bilayered-hydrate $Na_xCoO_2 \cdot yH_2O$ sample by a Co Nuclear Quadrupole Resonance (NQR) measurement. The nuclear spin-lattice relaxation rate divided by temperature $1/T_1T$ shows a prominent peak at 5.5 K, below which a Co-NQR peak splits due to an internal field at the Co site. From analyses of the Co NQR spectrum at 1.5 K, the internal field is evaluated to be ~ 300 Oe and is in the ab-plane. The magnitude of the internal field suggests that the ordered moment is as small as $\sim 0.015\ \mu_B$ using the hyperfine coupling constant reported previously. It is shown that the NQR frequency ν_Q correlates with magnetic fluctuations from measurements of NQR spectra and $1/T_1T$ in various samples. The higher-ν_Q sample has the stronger magnetic fluctuations. A possible phase diagram in $Na_xCoO_2 \cdot yH_2O$ is depicted using T_c and ν_Q, in which the crystal distortion along the c-axis of the tilted CoO_2 octahedron is considered to be a physical parameter. Superconductivity with the highest T_c is seemingly observed in the vicinity of the magnetic phase, suggesting strongly that the magnetic fluctuations play an important role for the occurrence of the superconductivity.

KEYWORDS: superconductivity, hydrate sodium cobalt oxide, NQR, spin fluctuations

Since the discovery of superconductivity in the bilayered-hydrate (BLH) $Na_xCoO_2 \cdot yH_2O$ (NCO) by Takada *et al.*,[1] a lot of works have been performed to investigate physical properties of this superconductivity. Different from the CuO_2 square lattice in cuprate superconductors, the CoO_2 plane, in which superconductivity in BLH NCO occurs, is formed by a triangular lattice. The geometrical frustrations inherent to the triangular lattice have been invoked to play a role for the occurrence of the superconductivity.

The crystal structure of BLH NCO consists of double hydrate layers sandwiching a Na

*E-mail address: ihara@scphys.kyoto-u.ac.jp
†E-mail address: kishida@scphys.kyoto-u.ac.jp

layer and two-dimensional CoO_2 block layers, in which CoO_6 octahedra are tilted and connect each other by edge sharing. In the presence of the distortion along the c-axis in the tilted CoO_6 octahedron, three degenerated t_{2g} orbitals are lifted and split into doublet e'_g orbitals and a singlet a_{1g} orbital. From a theoretical point of view, it is suggested that e'_g character which forms six hole-like Fermi surface near K point plays an essential role for the occurrence of the unconventional superconductivity.[2–4] However, these hole pockets are not observed by angle-resolved photo-emission spectroscopy (ARPES) studies in Na_xCoO_2 without water.[5,6] It is a crucial issue to experimentally determine which orbitals, the e'_g orbitals or a_{1g} orbital, are active for the superconductivity in BLH NCO.

Quite recently, a non-superconducting (SC) sample with BLH structure has been reported by Sakurai *et al.* We are interested in the electronic state in the non-SC BLH sample, especially how the electronic state is different from that in the SC BLH sample. This study might give a clue to know what is important for the superconductivity. From Co-Nuclear Quadrupole Resonance (NQR) measurements, we found a magnetic order in the non-SC BLH NCO sample. The transition temperature T_M is 5.5 K, which is very close to the highest-T_c ($T_c \sim 4.7$ K) in the BLH NCO system. Our finding shows that the superconductivity is realized near the magnetic phase, suggesting strongly that the electron correlations, especially magnetic ones are essential for the superconductivity.

Three samples we report here are listed in Table 1, together with the samples used in the previous studies.[7,8] In Table 1, values of T_c, Na content x and c-axis lattice parameter are shown. Details of preparation of these samples were reported elsewhere.[9] These samples are carefully characterized using an X-ray diffraction and the Na content was determined by inductively coupled plasma atomic-emission spectrometry (ICP-AES).

Table 1 signals that there is some relation between T_c and c-axis constant in SC samples, as suggested previously.[8,10,11] It is to be noted that x value is hardly correlated to T_c.[8,10] We consider that the superconducting properties are determined mainly by hydrate content,

No.	T_c	c	x	NQR frequency	Ref.
No.1	4.7 K	19.68 Å	0.348	12.30 MHz	[7]
No.2	4.6 K	19.72 Å	0.339	12.30 MHz	[8]
No.3	2.8 K	19.57 Å	0.348	12.08 MHz	
No.4	4.6 K	19.60 Å	0.35	12.32 MHz	
No.5	0 K	19.75 Å	0.331	12.54 MHz	

Table I. List of samples used for our NMR measurements. T_c, c and x are the SC transition, c-axis lattice constant and Na content, respectively. NQR frequency is the peak frequency of the NQR spectrum arising from the $\pm 5/2 \leftrightarrow \pm 7/2$ transitions (see in Fig.1).

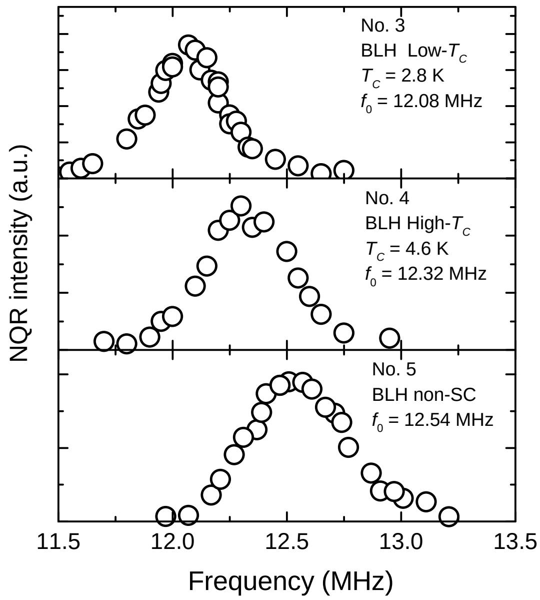

Fig. 1. NQR spectra arising from the $\pm 5/2 \leftrightarrow \pm 7/2$ transition in several samples with different T_c.

which is related with the c-axis lattice parameter.

Figure 1 shows Co-NQR spectra arising from the $\pm 5/2 \leftrightarrow \pm 7/2$ transition. We observed a single peak arising from the transition although Na ions partially occupy the Na layer. The double-hydrate layers screen the randomness of the Na layer, which is considered to be important for the superconductivity. The resonance frequency of this transition ν_Q strongly depends on samples, especially the c-axis lattice parameter. The ν_Q of the sample with $T_c \sim 4.6$ K is nearly the same as that of previous samples with the same T_c, indicative of ν_Q being reproducible. This suggests that ν_Q can be one of the good parameters to show physical properties of each sample with different T_c.

In general, ν_Q is determined by the electric field gradient (EFG) along the principal axis V_{zz}, (in this system, the c axis is the principal axis) and the asymmetric parameter η at the Co site. From measurements of the resonance frequencies at other transitions, it was revealed that η was nearly unchanged ($\eta = 0.208 \pm 0.007$) and ν_Q was changed by V_{zz}. Taking into account that the longer c-axis sample has the higher ν_Q, we suggest that the change of V_{zz} is related with the lattice distortion. It is noteworthy that the non-SC BLH sample has a higher ν_Q than that in other SC samples.

Next we measured nuclear spin-lattice relaxation rate $1/T_1$ to investigate spin dynamics in these samples. T_1 was measured at the NQR peaks shown in Fig.1, and can be determined by a single component in the whole temperature range. Figure 2 shows the temperature dependence of $1/T_1T$ of these samples, together with that of the mono-layered hydrate (MLH) NCO sample showing non-SC behavior and that of the BLH-NCO with $T_c \sim 4.7$ K (No.1) for comparison.[7] The Korringa ($1/T_1T$ = const.) behavior was observed in the MLH sample, indicative of

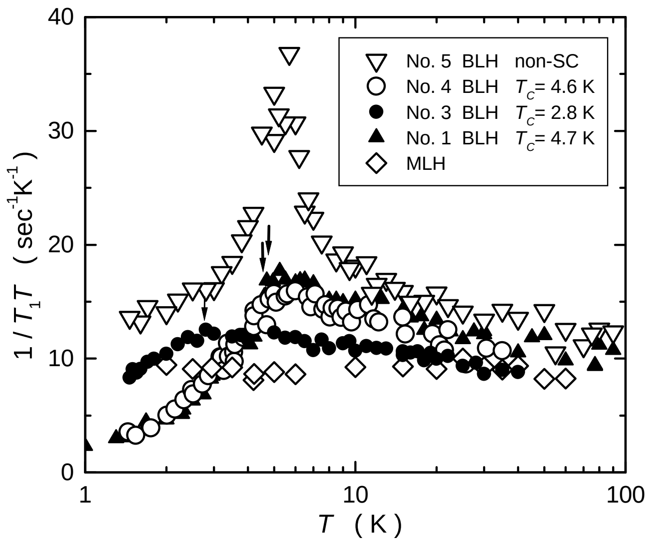

Fig. 2. Temperature dependence of $1/T_1T$ in various BLH NCO samples (No.3, 4,and 5) together with that in the non-SC MLH NCO sample and the SC BLH NCO sample with $T_c \sim 4.7$ K (No.1).[7] The arrows show T_c in samples.

absence of the temperature dependent magnetic fluctuations. In SC samples, the value of $1/T_1T$ increases with decreasing temperature from 50 K to T_c, and the value of $1/T_1T$ at T_c is larger in the higher-T_c sample. These behaviors are in good agreement with the previous results.[7,8] The remarkable finding is that $1/T_1T$ of the non-SC BLH sample shows a prominent peak at $T_M \sim 5.5$ K, suggestive of occurrence of a magnetic ordering. $T_M \sim 5.5$ K is close to the SC transition temperature T_c. $1/T_1T$ above T_M is larger than that in other SC samples, indicating that magnetic fluctuations in the non-SC BLH sample are stronger than those in the high-T_c sample. It should be noted that the temperature dependence of $1/T_1T$ is the same for the non-SC sample and the high-T_c sample in the temperature range of 10 - 100 K. These experimental results suggest strongly that the unconventional superconductivity in the BLH NCO occurs in the vicinity of the magnetic ordering, and that the magnetic fluctuations in the high-T_c sample are close to the magnetic instability.

In order to know the magnetically-ordered state, NQR spectra arising from all the transitions are obtained. Figure 3 shows the NQR spectra above (8 K) and below (1.5 K) T_M. Three single peaks corresponding to the $\pm 1/2 \leftrightarrow \pm 3/2$ (4.90 MHz), $\pm 3/2 \leftrightarrow \pm 5/2$ (8.20 MHz), and $\pm 5/2 \leftrightarrow \pm 7/2$ (12.54 MHz) transitions are observed at 8 K. At 1.5 K below T_M, the peaks at 4.90 MHz and 12.54 MHz becomes slightly broader, whereas the peak at 8.20 MHz splits into two peaks asymmetrically. It seems that the effect of the internal field appears mainly in the $\pm 3/2 \leftrightarrow \pm 5/2$ transition.

In general, the NQR Hamiltonian with an internal field $\overrightarrow{H} = (H_x, 0, H_z)$ is expressed as,

$$\mathcal{H} = \frac{\hbar\nu_z}{6}\{3I_z^2 + I^2 + \eta(I_+^2 + I_-^2)\} + \gamma\hbar(I_xH_x + I_zH_z)$$

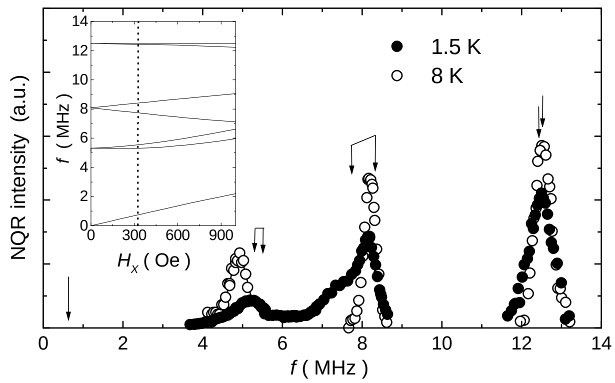

Fig. 3. Co NQR spectra of 1.5 K (black) and 8 K (white). The transition of 8.2 MHz is largely affected by the internal field. The inset shows the dependence of transition frequencies arising from all transitions with respect to the change of the internal field along the CoO_2 plane H_x. The peaks at 1.5 K are interpreted by $H_x \sim 300$ Oe. The calculated peaks are shown by arrows in the main figure.

Here ν_z is defined as $\nu_z = 3eQV_{zz}/3I(2I-1)$ with Q being the nuclear quadrupolar moment, and the asymmetric parameter η is $|\nu_x - \nu_y|/\nu_z$. If H_z were dominant, all transitions would be affected by the operator I_z. Obviously this is not the case. The inset shows calculated curves of three-transition frequencies with respect to the change of an internal field along the plane H_x, in which the experimental data of $\nu_z \sim 4.2$ MHz and $\eta \sim 0.203$ evaluated from the NQR spectra above T_M are used. As seen in the inset, the transition at 8.20 MHz is largely affected by H_x. The NQR spectrum peaks at 1.5 K are consistently fitted by $H_x \sim 300$ Oe as shown in the inset. The asymmetric spectra at $\sim$ 8.2 MHz are interpreted by the difference of the transition probability of two split peaks. From the internal field at the Co site, the ordered moment is evaluated as small as 0.015 μ_B by using the hyperfine coupling constant being $\sim$ 20 kOe/μ_B derived from the K - χ plot in the normal state.[12]

To know the volume fraction of the ordered state and the temperature dependence of the ordered moments, the NQR spectra from the $\pm 5/2 \leftrightarrow \pm 7/2$ transition were obtained at various temperatures. Figure 4 shows the NQR spectra below 8 K. The insets (a) and (b) are the temperature dependence of the integrated intensity and the full width at half maximum (FWHM) of the NQR spectra, respectively. Due to the divergence of $1/T_1T$, the integrated intensity shows a minimum at 5.5 K, below which FWHM becomes broader. The temperature dependence of FWHM shows the mean-field-type behavior. It should be noted that the integrated intensity of the spectrum recovers totally at 1.5 K. This experimental fact excludes the possibility that some magnetic fraction is missing due to the occurrence of the large internal field, rather suggests that the weak magnetism in which the ordered moments are approximately $10^{-2}\mu_B$ occurs in the entire region of the non-SC BLH sample.

In order to consider what kind of a magnetic order occurs, we discuss the temperature

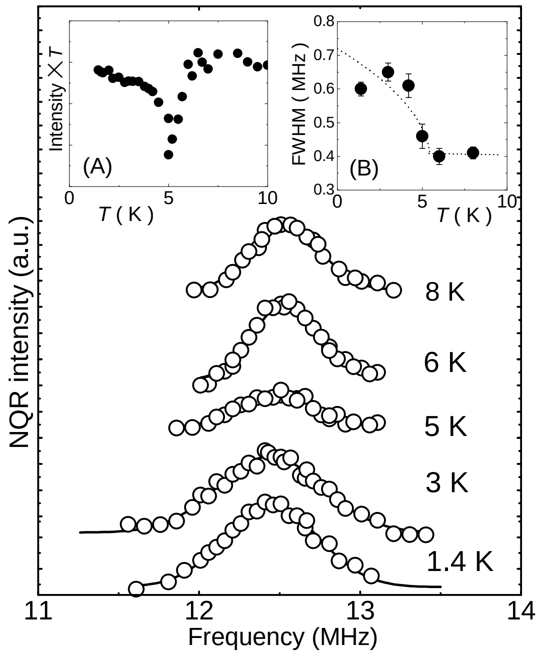

Fig. 4. Co-NQR spectra from the $\pm 7/2 \leftrightarrow \pm 5/2$ transition at various temperatures in the non-SC BLH sample. The inset (a) and (b) show the temperature dependence of the integrated intensity and the full width at half maximum (FWHM) of the spectrum, respectively. The dotted curves in the inset shows the mean-field-behavior, $\sim (1 - (T/T_M))^{1/2}$.

dependence of the bulk susceptibility $\chi_{\rm bulk}$ of the non-SC BLH sample. Figure 5 shows the temperature dependence of $\chi_{\rm bulk}$ of the powder sample measured at 10 kOe. A clear anomaly is observed at $T_M \sim 5.5$ K, below which $\chi_{\rm bulk}$ shows an upward increase below T_M. In typical antiferromagnetic (AFM) compounds $\chi_{\rm bulk}$ shows a peak at T_M, while, $\chi_{\rm bulk}$ diverges in ferromagnetic (FM) compounds. The inset of Fig. 5 shows the temperature dependence of $\chi_{\rm bulk}$ under a small field of 10 Oe. Tiny hysteresis was observed between zero-field-cooled (ZFC) and field-cooled (FC) measurements. This behavior might exclude the occurrence of the spin-glass and/or cluster-glass transition since a large hysteresis between FC and ZFC would be observed due to a spin freezing in these cases. The upward increase observed in the non-SC BLH sample can not be interpreted by ordinary magnetic anomaly, and therefore deserves to be clarified by further experiments.

Finally, we propose a possible phase diagram of $\mathrm{Na}_x\mathrm{CoO}_2 \cdot y\mathrm{H}_2\mathrm{O}$ using the experimental value of ν_Q as a tuning physical parameter in Fig.6. It is obvious that the magnetic phase is adjacent to the superconducting phase, although the relation and boundary between the two phases are not clear yet. If the superconductivity were induced by the electron-phonon mechanism, the superconductivity would be suppressed by strong magnetic fluctuations close to the magnetic instability. Instead, taking into account that the SC transition temperature smoothly changes into the magnetic-ordering temperature, we suggest that the magnetic fluc-

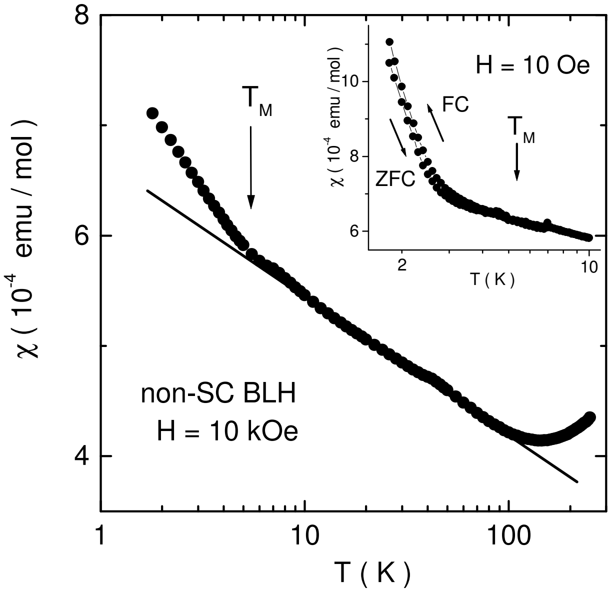

Fig. 5. Temperature dependence of magnetic susceptibility $\chi_{\rm bulk}$ in the non-SC BLH samples measured in $\sim$ 20 kOe. Horizontal axis is a logarithmic scale. Anomaly is observed at 5.5 K, below which $\chi_{\rm bulk}$ shows an upward increase. The inset shows $\chi_{\rm bulk}$ measured in a small field of 10 Oe.

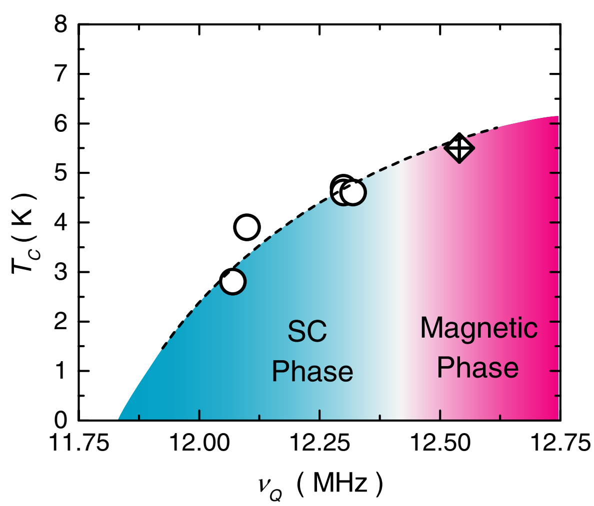

Fig. 6. Proposed phase diagram of $Na_xCoO_2 \cdot yH_2O$. The vertical and horizontal axes are transition temperature and resonance frequency ν_Q, respectively. The boundary between SC and magnetic phases seems to be present around 12.4 MHz. The data in Ref. [8] are also plotted.

tuations which induce the magnetic ordering might be related with the superconductivity.

Now, we consider physical meaning of the tuning parameter ν_Q. As discussed above, ν_Q is determined by the EFG along the c axis, V_{zz} which is related with the crystal distortion of the CoO_2 block layers. In addition, it was reported from the neutron-scattering experiment

that the strong inverse correlation between the CoO_2-layer thickness and T_c (T_c increases with decreasing the thickness).[13] Taking into account these experimental results, we consider that a decrease of the layer thickness, which makes ν_Q larger, corresponds to a compression of the tilted octahedron along the c axis. Such a distortion makes the three degenerated t_{2g} orbitals futher split into one a_{1g} and two e_g' orbitals. According to theoretical calculations, hole-character Fermi surface (FS) of the six hole pockets, which are formed by the e_g' orbitals (e_g'-FS), becomes larger when the compression along the c axis becomes larger.[14] Therefore, we consider that the change of the parameter ν_Q corresponds to change of the e_g'-FS volume. It was reported from the theoretical calculation that the static spin susceptibility around the Γ point is enhanced and the spin-triplet superconductivity with p- or f-wave character is stabilized when the e_g'-FS volume becomes larger.[4] In this meaning, the spin fluctuations, which are enhanced when ν_Q becomes larger, might have a ferromagnetic character. However, a crucial discrepancy was reported: spin-singlet superconductivity was suggested by Co-Knight shift measurements.[15] One of the most important questions to be answered is how the spin fluctuations around the Γ point, which is close to the magnetic instability, can coexist with spin-singlet superconductivity. Further experiments are still needed to clarify the SC and spin-fluctuation nature in the BLH NCO system.[16]

In conclusion, we found the weak magnetic order below $T_M \sim 5.5$ K in a non-SC $Na_xCoO_2 \cdot yH_2O$ sample with the same structure as SC samples. The ordered moment is approximately 0.015 μ_B, which resides in the CoO_2 plane. The unusual upward increase was observed in $\chi_{\rm bulk}$ below T_M, which are different from behaviors observed below an ordinary magnetic transition. From NQR measurements on various BLH NCO samples with different T_c, we suggest that ν_Q could be a tuning parameter of the ground state in this system, and that the occurrence of the superconductivity might be related to the c-axis distortion of the tilted CoO_6 octahedron.

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